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(71) Applicant (*for all designated States except US*): DUPONT CANADA INC. [CA/CA]; Box 2200 Streetsville, Mississauga, Ontario L5M 2H3 (CA).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): NG, Howard, Chung-Ho [CA/CA]; 896 Nottinghill Avenue, Kingston, Ontario K7P 2B4 (CA). FARKAS, Nicholas, Akos [CA/CA]; 777 Kimberley Street, Kingston, Ontario K7P 1C2 (CA).

(74) Agent: McKAY, Judith, E.; Box 2200 Streetsville, Mississauga, Ontario L5M 2H3 (CA).

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(57) Abstract

Heat-sealable polyamide films or layers are formed from polyamides containing: (a) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and (b) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone. Additionally, heat-sealable films or layers can be formed from blends containing: (a) at least one polyamide containing: (i) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and (ii) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone; and (b) at least one polymer selected from polyamides, vinyl polymers, graft functionalized C_2-C_{20} alpha-olefin polymers, ethylene/ethylenically unsaturated carboxylic acid copolymers, or ionomers.

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TITLE

POLYAMIDES AND HEAT-SEALABLE FILMS FORMED THEREFROM

FIELD OF THE INVENTION

The present invention relates to heat-sealable polyamide (nylon) films and multilayered structures made therefrom for use in packaging. In particular, the invention relates to polyamide films and multilayered structures made therefrom which are suitable for packaging food and liquid products such as, but not limited to, fresh meat, processed meat, cheese, sausages, and milk.

BACKGROUND OF THE INVENTION

Nylon is the generic name for a family of polyamides characterized by the presence of the amide group -CONH. The utility of nylon compositions and products are well-known with everyday examples including usage in packaging, brushes, and tires, as synthetic films, fibers, plastics and molding resins.

Thermoplastic flexible films are used in a wide variety of applications including bags (e.g. for merchandise, leaves, garbage, etc.), wrappings for industrial packaging, in electrical and electronic uses, as communications media substrates, adhesive coated products such as tapes and labels, medical packaging, and food packaging.

In the food industry, thermoplastic flexible films are used to keep food fresh prior to consumption. Greater use of centralized processing of foods in conjunction with increased handling and longer delivery times associated with long distance transportation have increased the demand for packaging films having superior properties.

In the poultry and meat segments of the food industry thermoplastic flexible films are utilized to maintain freshness. Meat is frequently sold fresh, frozen or cooked; therefore films advantageously provide protection at various temperatures. Food items such as primal and subprimal cuts of beef, ground beef and processed meats are known to use coextruded or laminated films which utilize such compositions as nylon, polyester, copolymer of vinylidene chloride (PVDC), ethylene-vinyl acetate copolymer (EVA) and ionomers.

It is also generally known that selection of films for packaging food products includes considerations such as, but not limited to, barrier properties, cost, durability, puncture resistance, flex-crack resistance, FDA approval, machinability, optical properties such as gloss and haze, printability, shrinkability, shrink force, stiffness, and

strength. Additionally, it is desirable that the films or structures have good heat seal properties.

In general, nylon films are made by processes which include casting or blown film and these films may be uni-or biaxially oriented. Polymers of aliphatic dicarboxylic acids and mixtures of aliphatic diamines having 4-12 carbon atoms with 2-methyl pentamethylene diamine have been disclosed in published PCT patent application No. WO 92/12194 of N. Farkas, D.N. Marks and S.M. Nemser, published 1992 July 23. Specific types of nylon such as nylon 6, nylon 6,6, and nylon 12 have been made into films. Known advantages of nylon films relative to other film materials in packaging applications include good oxygen and flavor barrier characteristics, durability at low temperatures and thermal stability. However, nylons in general are poor moisture barriers. Further, polyamides such as nylon 6 and nylon 6,6 have sharp, narrow crystalline melting points, and therefore it is difficult to control a process for the heat sealing together of two polyamide films. The seals obtained tend to be brittle.

Polyethylene film is widely used in the packaging industry in the form of both mono-layer and multi-layer films, including in the packaging of foodstuffs. In some embodiments, the polyethylene film is used as a monolayer film and heat-sealed to form packages or pouches e.g. for the packaging of milk. In embodiments of such end-uses, the polyethylene may be a copolymer of ethylene and butene-1, but more preferably is a copolymer of ethylene and octene-1. Important characteristics of polyethylene used to form pouches are that the heat seal strength is sufficient to obtain a pouch with good resistance to bursting in normal use and that, in the formation of pouches, the hot tack strength is sufficient to retain the packaged material while the seal is still hot. The measurement of heat seal strength and hot tack strength is described below, with the former being a measure of the strength of a heat seal when cool and the latter being a measure of the strength of the seal when still hot.

Polyethylene film provides a good moisture barrier but where other barrier properties are required e.g. barrier to oxygen, it is necessary to use polyethylene film in the form of laminates e.g. laminates with polyamide films, optionally including additional barrier layers. As stated above, polyamide films provide barrier properties

to gases, but monolayer polyamide films, especially those formed from nylon 6 or nylon 66 and related copolyamides, lack adequate heat seal strength and moisture barrier properties.

Due to recent growth in the market for barrier films, there currently exists an industry wide need for films with more balanced properties including barrier properties such as low oxygen permeability and low moisture permeability as well as good heat-sealability. For packaging applications in which the package provides not only containment of the products but also barrier properties, multilayer films are commonly employed to utilize the most beneficial properties of the various film layers because no one polymer has been recognized, until now, to possess a balance of properties necessary to satisfy the marketplace's demands.

~~The present invention provides films and multilayer structures~~ made from certain polyamides or polymer blends, which ameliorate many problems associated with known films as discussed above. More specifically, the present invention provides polyamides and polymer blends which can be formed into films or multilayered structures with more balanced properties including barrier properties such as low oxygen permeability and low moisture permeability as well as good heat-sealability. Thus, the present invention combines the heat-sealability of a polyolefin with the desirable properties of polyamides typically used in packaging applications, i.e. nylon 6 or nylon 6,6. In addition, the polyamide films of present invention exhibit a good balance of barrier properties.

SUMMARY OF THE INVENTION

The present invention relates, in part, to a heat-sealable polyamide film formed from a polyamide comprising:

(a) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and

(b) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone.

Further, the present invention relates, in part, to multilayered structures comprising the heat-sealable film of the present invention. The multilayered structures

can be prepared by lamination, coextrusion, extrusion coating or a combination of these techniques.

Finally, the present invention relates, in part, to a heat-sealable film formed from at least one polyamide described herein blended with at least one of nylon 6, nylon 66, graft functionalized C_2-C_{20} alpha-olefin polymer, ethylene/ethylenically unsaturated carboxylic acid copolymers and ionomers.

BRIEF DESCRIPTION OF DRAWINGS

In the drawings:

Fig. 1 shows a DSC melting point profile as measured using the procedure of ASTM D-3418 for several copolyamides;

Fig. 2 shows a DSC melting point as measured using the procedure of ASTM D-3418 of a polyamide prepared from sebacic acid and 2-methyl-pentamethylene diamine;

Fig. 3 shows a DSC melting point as measured using the procedure of ASTM D-3418 of another polyamide prepared from dodecanedioic acid and 2-methyl-pentamethylene diamine;

and Fig. 4 shows a representative profile for a heat seal or hot tack bond strength vs. seal temperature.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates, in part, to a heat-sealable polyamide film formed from a polyamide comprising:

(a) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and

(b) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone.

The heat-sealable polyamide film of the present invention exhibits sufficient heat seal and/or hot tack bond strength to enable the film to be used as a monolayer film or container or the like, or as a heat seal layer of multilayered structures in end-uses involving heat sealing. In this application the heat seal or hot tack bond strength is the maximum bond strength measured in the sealing temperature

range of the polyamide film, i.e., from the initial sealing temperature to the temperature at which the film starts to melt. This maximum bond strength corresponds to the plateau seal strength as shown in Fig. 4. For the purpose of determining maximum bond strength, the test should preferably be done at about 5°C temperature intervals in the film's sealing temperature range. It will be understood that by "initial" sealing temperature, the present inventors are referring to the minimum temperature at which a minimum detectable bond strength is observable.

In one embodiment, the present invention provides a heat-sealable polyamide film having a heat seal strength of greater than about 50 g/cm, a hot tack strength of greater than about 10 g/cm, a heat seal initiation temperature of less than about 140°C and a hot tack initiation temperature of less than about 170°C. The heat-sealable film of the present invention will preferably exhibit a heat seal strength of greater than about 80 g/cm, more preferably greater than about 100 g/cm, and most preferably greater than about 200 g/cm. The heat-sealable film of the present invention will preferably exhibit a hot tack strength of greater than about 15 g/cm, more preferably greater than about 25 g/cm, and most preferably greater than about 40 g/cm. The heat-sealable film of the present invention will preferably exhibit a heat seal initiation temperature of less than about 135°C. The heat-sealable film of the present invention will preferably exhibit a hot tack initiation temperature of less than about 155°C. Additionally, the heat-sealable film of the present invention will exhibit an oxygen transmission rate of less than about 60 cc-mil/100 in^2 /day as determined according to ASTM-3985-81.

The heat seal initiation and hot tack initiation temperatures used herein are measured at the interface between the layers, not in the jaw of the sealing apparatus. Such temperatures will be different from temperatures measured in the heat sealing jaw of heat sealing apparatus, especially if only one jaw of such apparatus is a heated jaw. In tests, the temperature between the upper jaw of a Sentinal heat sealer and the film adjacent thereto as well as the temperature between the lower jaw and the film adjacent thereto were measured; only the upper jaw was a heated jaw. The two measured temperatures were averaged and the average was deemed to be the temperature at the interface between the films. That temperature was compared with

the temperature measured by a thermocouple in the upper jaw, that thermocouple being used in the control of the temperature of the upper jaw to a set temperature. Under these circumstances, a substantial difference in temperatures was observed. For instance, when the interface temperature was 86°C, 125°C and 202°C, the jaw temperature was 110°C, 170°C and 260°C, respectively. These differences will be particularly dependent on various factors including, but not limited to, the sealing apparatus used, whether one or both jaws are heated, and the location of the thermocouple in the jaw. For that reason, interface temperatures are specified herein.

The heat-sealable polyamide film may be formed by a cast film process or by a blown film process. Both types of film processes are known in the art of manufacture of polyamide films. Furthermore, the film may be a monolayer film or a multilayer film, the film being for example a coextruded film or a laminate. Either the monolayer film or the coextruded film may be in an unoriented condition, in the form of monoaxially oriented film or in the form of biaxially oriented film. It will be understood by persons skilled in the art that the properties of such polyamide films will depend on several factors including, but not limited to, extruder hold-up time and screw design, melt processing temperature, quenching rate and degree of quenching, film thickness, the amount of and type of additional components, as well as the amount of and type of the particular polyamide as described herein.

In the embodiment in which the film is a coextruded film, the polymer used in the coextrusion with the polyamides defined herein may, in preferred embodiments, be a heat-sensitive polymer composition, particularly heat-sensitive polymer compositions that will degrade when subjected to the temperatures required for the extrusion of nylon 6 or especially nylon 6,6 polyamide. Examples of such heat-sensitive polymer compositions include polyvinyl alcohol (PVOH) or ethylene/vinyl alcohol copolymers (EVOH) which have a decomposition temperature of about 200°C and 240°C, respectively, and ethylene/vinyl acetate copolymers which have a decomposition temperature of about 220°C. The polyamides described herein may also be coextruded or laminated with polyolefins or grafted polyolefin, particularly polyethylene, grafted polyethylene or grafted polypropylene, especially using tie or adhesive layers between the polyamide and polyolefin. The heat-sealable

polyamide films may be laminated to polyolefins or other barrier polymers using conventional processes. In addition, the heat-sealable polyamides may be coated with polyvinylene dichloride(PVDC), EVOH, PVOH or other suitable barrier coatings and then laminated to itself to form a higher barrier heat-sealable structure.

The heat-sealable polyamide films of the present invention may be used in the form of packages, including puoches bags, etc. In particular, the packages may be used in the packaging of food and liquid products. For instance, the polyamide film may be fed to a vertical form, fill and seal apparatus of the type used in the packaging of milk or other flowable materials. In such embodiments, the package would be in the form of a pouch.

The polyamides used to form the heat-sealable polyamide film of the ~~present invention are prepared from~~

(a) at least one dicarboxylic acid and at least one diamine, wherein said dicarboxylic acid or said diamine or both contain at least one alkyl branch having one to three carbon atoms; and wherein said dicarboxylic acid or said diamine or both comprise at least seven methylene groups; or

(b) at least one alpha, omega aminocarboxylic acid, having the formula of H_2N-R(1)-COOH, in which R(1) is an aliphatic moiety having at least six methylene groups and at least one pendant alkyl branch having 1 to 3 carbon atoms, or

(c) at least one diamine and at least one nitrile selected from the group consisting of alpha omega amino alkylene nitriles and alpha omega alkylene dinitriles, wherein said diamine or said nitrile or both contain at least one alkyl branch having one to three carbon atoms; and wherein said diamine or said nitrile or both comprise at least seven methylene groups; or

(d) mixtures of any of the monomers described in (a)-(c) above.

Examples of the diamines include 1,6 hexamethylene diamine; 1,8 octamethylene diamine; 1,10 decamethylene diamine and 1,12-dodecamethylene diamine. Examples of a branched diamine include 2-methyl-pentamethylene diamine, but other branched diamines having C1-C3 alkyl branches may be used.

Examples of the dicarboxylic acids include 1,6-hexanedioic acid (adipic acid); 1,7-heptanedioic acid (pimelic acid); 1,8-octanedioic acid (suberic acid); 1,9-nonanedioic acid (azelaic acid); 1,10-decanedioic acid (sebacic acid) and 1,12-dodecanedioic acid. Examples of branched dicarboxylic acids include 2-methyl glutaric acid, but other branched dicarboxylic acids having C_1-C_3 alkyl branches may be used.

Examples of alpha, omega amino carboxylic acids are aminocaproic acid, amino octanoic acid, amino decanoic acid, amino undecanoic acid and aminododecanoic acid. It should be noted that the aminocarboxylic acid may be in the form of a lactam, especially when the aliphatic moiety has six methylene groups. Examples of branched alpha, omega amino carboxylic acids are 2-methyl-amino dodecanoic acid and 2-methyl-amino decanoic acid although others may be used.

Examples of the nitriles are 1,5 aminocapronitrile, adiponitrile, 1,11-amino undecanonitrile, 1,10-amino decanodinitrile and 2-methyl-1,11-amino undecanonitrile although others may be used.

In addition to monomers (a)-(c) listed herein, other monomers may be used to prepare the polyamides of the present invention. These other monomers include, but are not limited to, aromatic dicarboxylic acids, aromatic diamines, alicyclic dicarboxylic acids, and alicyclic diamines. Examples of aromatic dicarboxylic acids include terephthalic and isophthalic acids. An example of an alicyclic dicarboxylic acid is 1,4-bismethylene cyclohexyl dicarboxylic acid. An example of an alicyclic diamine is 1,4-bismethylene diamino cyclohexane.

Depending on the combination of monomers used, the polyamides of the present invention can be semi-crystalline or amorphous. When the polyamide is semi-crystalline, it is desirable that such polyamide exhibit a melting point less than or equal to about 180°C and a broad melting profile, which is herein defined as the range of temperature from the onset of the melting curve in a differential scanning calorimetry (DSC) test to the maximum melting peak that is measured, of greater than about 45°C.

The polyamides may be manufactured using processes well known in the art. In particular the polyamides may be polymerized from salts of the diamine and

dicarboxylic acid. Alternatively the polyamides may be polymerized using the corresponding nitriles, as discussed above.

The polyamide may be in the form of a homopolymer polymerized from one diamine and one dicarboxylic acid, an aminocarboxylic acid, an amino alkyl nitrile, or one diamine and a dinitrile. Alternatively, the polyamide may be a copolymer polymerized from at least one diamine with more than one dicarboxylic acid or at least one dicarboxylic acid with more than one diamine or a combination of at least one diamine, at least one dicarboxylic acid and at least one aminocarboxylic acid, optionally containing nitriles. The copolymer preferably contains at least about 20 mole percent of branched moieties, more preferably at least about 30 mole percent and most preferably at least about 50 mole percent of branched moieties, based on the ~~total amount of the aliphatic moieties in the polyamide~~.

In preferred embodiments of the present invention, the polyamide, when semi-crystalline, has a melting point of less than or equal to about 180°C, more preferably between about 120°C to about 180°C, and most preferably between about 140°C to about 180°C. It is also preferred that the polyamide has a broad melting profile of greater than about 45°C, preferably greater than about 50°C, and most preferably greater than about 55°C.

The polyamide may also have a broad crystal morphology, defined as multiple melting points covered under a single broad melting profile or two overlapping melting peaks not separated by more than 20°C in a differential scanning calorimetry test. Thus, it is less desirable for the polyamide to have a sharp melting point but rather it is desirable for the polyamide to have the characteristic of melting over a broad temperature range in order to provide heat seals with acceptable strength. Melting points referred to herein were determined using the procedure of ASTM D-3418 (1988) using a DuPont DSC Instrument Model 2100; the heating and cooling rates were 10°C/min.

In addition to being in the form of a film, the polyamides may be in a form of a layer, in particular a coating. In such an embodiment, the polyamide could be a coating on another substrate, particularly a flexible substrate. For example, the flexible substrate could be a polyester film, a polyamide film, a polyethylene film, or a

polypropylene film. Additionally, the polyamides may be used in rigid or semi-rigid containers (i.e. as a coating on the inside of the container), or in medical packaging or industrial end-uses. Industrial end-uses could include use as a heat-sealable release film, for example when the polyamide is blended with a grafted polymer.

The polyamides of the present invention, especially when in the form of layers e.g. films or coatings, may be treated with a corona discharge (ED) in order to improve the properties of the polyamide with respect to bonding of coatings, inks, adhesives or the like. In addition, the polyamides may contain additives such as, but not limited to, moisturizing agents, heat stabilizers, flame retardants, fillers, anti-blocking agents, slip additives, pigments or dyes, processing aids, anti-oxidants, plasticizers or ultra violet blocking agents.

The present invention further relates, in part, to a heat-sealable film formed from at least one polyamide described herein blended with at least one polymer selected from the group consisting of polyamides, vinyl polymers, graft functionalized C_2-C_{20} alpha-olefin polymers, ethylene/ethylenically unsaturated carboxylic acid copolymers and ionomers. In one embodiment, these heat-sealable films will have a heat seal initiation temperature of less than about 140°C. By blending the polyamides described herein with one or more of the polymers listed above, various improvements in film properties can be achieved such as, but not limited to, reduction in film blocking properties, toughness, and barrier properties.

The blends may be in the form of a polyamide defined herein blended with at least one polymer selected from the group consisting of polyamides; vinyl polymers such as PVC, EVOH and PVOH; graft functionalized C_2-C_{20} alpha-olefin polymers; ethylene/ethylenically unsaturated carboxylic acid copolymers and ionomers, including Fusabond® graft copolymers from DuPont Canada Inc. and Nucrel® copolymers and Surlyn® ionomers from E.I. du Pont de Nemours and Company. In particular, the blends should contain at least about 40 weight percent, and preferably at least about 50 weight percent, of the polyamide defined herein.

The graft monomers, and mixtures thereof, used to prepare the graft polymers can be selected from the group consisting of ethylenically unsaturated acidic monomers or their derivatives including acrylic acid, methacrylic acid, maleic acid,

fumaric acid, itaconic acid, crotonic acid, 5-norbornene-2,3-dicarboxylic acid, maleic anhydride, monosodium maleate, disodium maleate, itaconic anhydride, citraconic anhydride, monomethyl fumarate and monomethyl maleate. Also, the graft monomers can be selected from ethylenically unsaturated monomers containing amino or hydroxy functional groups including vinyl pyridines, vinyl silanes, 4-vinyl pyridine, vinyltriethoxysilane and allyl alcohol. The grafting monomers, and mixtures thereof, can be present in the graft polymer in an amount of from 0.05 to 5% wt. and would be grafted onto a C_2-C_{20} polyolefin including polyethylene, polypropylene, ethylene propylene diene terpolymer, as well as copolymers of ethylene with, but not limited to, vinyl acetate, carbon monoxide, or ethylenically unsaturated carboxylic acids or esters thereof.

TEST METHODS

In the heat seal test referred to herein, the heat seals were obtained using a Sentinal (Model 12AS) heat sealer, using a 10 cm wide sample, 138 KPa jaw pressure, 0.25 second set-point dwell time during sealing (actual jaw closure time measured to be 0.3-0.4 seconds) and a 0.25 inch (0.64 cm) wide sealing bar. On this type of heat sealer, only the upper jaw is heated, that jaw being heated continuously. Three pre-heat cycles (jaw closures) were done to pre-heat the lower jaw prior to the heat seal test. Samples were cut having a width of 0.5 inches (1.25 cm) and tested on a Suter tester at a jaw separation rate of 30-40 cm/min free fall; the tail of the sample was kept perpendicular to the direction of pull; or the samples were tested on a Instron (Model 4204) having a crosshead speed of 12 inches (30.5cm) per minute and having a grip distance of 2 inches (5.08 cm).

In the hot tack test referred to herein, a loop of the film 3 inches (7.6 cm) wide was formed with a known weight hanging from the loop. (For Examples I-III, the maximum weight available for hot tack tests was 800 g, while a 1400 g weight was available for Examples VII and VIII.) The film was then sealed to itself using a Sentinal heat sealer (Model 1212AS or 12AS) at a pre-determined temperature and a 138 KPa jaw pressure, using a dwell time (jaw closure time) of one second and a one inch (2.54 cm) wide sealing bar. Only the upper jaw was heated on this heat sealer, that jaw being heated continuously. Two pre-heat cycles (jaw closures) were done to

pre-heat the lower jaw before the test. The film sample was removed from the heat sealer and the integrity of the seal was immediately determined, the weight actually being activated 0.5 seconds into the dwell time of one second; a separation of 1 mm or less in the seal, caused by the weight on the seal while still hot, was deemed to be acceptable. The procedure was then repeated to determine the weight at which a separation of 1 mm was obtained; this latter weight was deemed the maximum hot tack strength. The procedure was repeated at different temperatures.

It is understood that heat seal and hot tack can be measured on any commercially available heat sealer. In the determination of minimum heat seal and hot tack temperatures described herein; the minimum heat seal strength measurable on the apparatus used was about 30 g/cm and the minimum hot tack strength measurable was about 10 g/cm.

EXAMPLES

The present invention is illustrated by the following examples.

Example 1

Pellets of a homopolymer of 2-methyl pentamethylene diamine and dodecanedioic acid (D,12) were melt extruded in a 1.90 cm Brabender single screw extruder at a temperature of 188°C and extruded through a 15 cm flat film die. The extrudate was quenched on a chill roll set at a temperature of 50°C to form a film having a thickness of 84 microns. The D,12 polymer had a relative viscosity of 51 (in formic acid) and a melting point of 149°C. A nylon 66 control resin, having a relative viscosity of 52 (in formic acid) and a melting point of 260°C, was extruded through the same extruder at a temperature of 292°C and quenched on a chill roll set at 50°C to form a film having a thickness of 86 microns.

Heat seal and hot tack tests were carried out on these films. In addition, a commercially availble linear low density polyethylene (LLDPE) film, Sclairfilm® LX-3, was also tested. The results reported in Table I show the temperatures at which the films began to heat seal and the temperatures at which the films exhibited their maximum heat seal strength, as well as the actual maximum heat seal strength. Similar data is provided for hot tack. The results obtained were as follows:

TABLE I

Polymer	Heat Seal Initiation Temp. (°C)	Temp. (°C) at Max. Heat Seal Strength	Heat Seal Maximum Strength (g/cm)	Hot Tack Initiation Temp. (°C)	Temp. (°C) at Max. Hot Tack Strength	Hot Tack Maximum Strength (g/cm)
D,12	70	90	1300	92	92-108	52
Nylon 66	200	200-210	236-1023	—	—	0
LLDPE	93	103	1220	92	107	79

The results show that the film made from the D,12 polymer exhibited both acceptable heat seal strength and hot tack strength, comparable to the LLDPE film, whereas the nylon 66 film exhibited heat seal strength at much higher temperatures and no hot tack strength.Example II

Pellets of a copolymer of dodecamethylene diamine and 2-methyl ~~pentamethylene diamine (40:60) and adipic acid (12,6/D,6 40:60)~~ were melt extruded in a 1.9 cm Brabender single screw extruder at a temperature of 206-212°C and extruded through a 15 cm flat film die. The extrudate was quenched on a chill roll set at a temperature of 49°C to form a film having a thickness of 84 microns. The 12,6/D,6 copolymer had a relative viscosity of 36 (in formic acid) and a melting point of 176°C. A nylon 66 control resin, having a relative viscosity of 52 (in formic acid) and a melting point of 260°C, was melt extruded in the same extruder at a temperature of 288°C-297°C and quenched on a chill roll set at 49°C to form a film having a thickness of 88.9 microns.

Heat seal and hot tack tests were carried out on these films.In addition, a commercially availble linear low density polyethylene (LLDPE) film, Sclairfilm® LX-3, was also tested. The results obtained were as follows:

TABLE II

Polymer	Heat Seal Initiation Temp. (°C)	Temp. (°C) at Max. Heat Seal Strength	Heat Seal Maximum Strength (g/cm)	Hot Tack Initiation Temp. (°C)	Temp. (°C) at Max. Hot Tack Strength	Hot Tack Maximum Strength (g/cm)
12,6/D,6 (40/60)	130	138-144	1023	130-152	144-180	65-105
Nylon 66	202	212	354	-	-	0
LLDPE	93	103	1220	92	107	79

The results show the comparable heat seal and hot tack properties of the 12,6/D,6 film and the LLDPE film. The results also show the superior heat seal and hot tack properties of the 12,6/D,6 film, as compared to the nylon 66 film.Example III

Pellets of a copolymer of dodecamethylene diamine and 2-methyl pentamethylene diamine (40:60) and adipic acid (12,6/D,6 40:60) were melt extruded in a 1.90 cm Brabender single screw extruder at a temperature of 204°C and extruded through a 15 cm flat film die. The extrudate was quenched on a chill roll set at a temperature of 49°C to form a film having a thickness of 88.9 microns. The 12,6/D,6 copolymer had a relative viscosity of 61 (in formic acid) and a melting point of 176°C. A nylon 66 control resin, having a relative viscosity of 52 (in formic acid) and a melting point of 260°C, was melt extruded in the same extruder at a temperature of 288°C-297°C and quenched on a chill roll set at 49°C to form a film having a thickness of 88.9 microns.

Heat seal and hot tack tests were carried out on these films. In addition, a commercially available linear low density polyethylene (LLDPE) film, Sclairfilm® LX-3, was also tested. The results obtained were as follows:

TABLE III

Polymer	Heat Seal Initiation Temp. (°C)	Temp. (°C) at Max. Heat Seal Strength	Heat Seal Maximum Strength (g/cm)	Hot Tack Initiation Temp. (°C)	Temp. (°C) at Max. Hot Tack Strength	Hot Tack Maximum Strength (g/cm)*
12,6/D,6 (40/60)	<134	144	1810	130	145-160	105
Nylon 66	202	212	354	---	---	0
LLDPE	93	103	1220	92	107	79

The results show the comparable heat seal and hot tack properties of the 12,6/D,6 film and the LLDPE film. Also, the results show the superior heat seal and hot tack properties of the 12,6/D,6 film, as compared to the nylon 66 film.Example IV

In this example, low melting copolyamides were prepared using an open vessel polymerization technique. The apparatus consisted of a round-bottom flask equipped with a jacketed Vigreaux reflux column, a mechanical stirrer and a distillation head with a Liebig take-off condenser. The condenser was fitted with a graduated fraction cutter and a distillate receiver. The apparatus was connected to nitrogen to permit purging. The polymerization flask was heated by an electrically heated mantle.

The following procedure was used for polymerization of copolyamides from aliphatic diamine, branched diamine and aliphatic dicarboxylic acids. Either dry salts f the diamines and acid or stoichiometric amounts of the reactants required to obtain the polymer composition were placed in the flask, and the flask was purged free of oxygen. With cold water in the Vigreaux column jacket, the flask was heated to 200°C with the stirrer operating. Over a period of about three hours, the amount of water generated by the condensation reaction and collected in the fraction cutter was approximately the theoretical amount for complete reaction. The temperature was raised to 220°C and the heating continued for another hour. The copolyamide formed had an IV (Inherent Viscosity, measured in m-cresol) of higher than 0.6. The polymer was cooled down to room temperature overnight.

Examples for the polymerization of different polymer compositions from 1,12-dodecane diamine (12), 2-methyl pentamethylene diamine (D) and adipic acid (6) are given in Table IV. For comparison, a 12,6 homopolyamide that had been made by the same procedure but finished at 240°C, is also included. The melting point profile of these copolyamides are given in the DSC scan as shown in Figure 1. Based on the criteria of relatively low melting point, broad melting profile and optimized morphology as discussed above, compositions of the copolyamides containing the branched diamine/aliphatic diacids between 50-60 mole percent seem to be the most desirable for heat sealable films; 12,6/D,6 (40/60) lies in this composition range and would be expected to be heat sealable.

Nuclear magnetic resonance analysis of the polymer showed that the polymer compositions were identical with the feed monomer composition, indicating that manufacture of a copolyamide of a specific composition can be controlled by feeding the corresponding monomer ratio to the reactor. The copolyamides were also synthesized in a larger autoclave and subjected to a vacuum finishing step to obtain higher molecular weight.

For instance, in the preparation of 12,6/D,6 (40/60), the following reactants were added, in order, to a 35L autoclave: 6.82 kg of water, 8.7 kg of adipic acid, 4,771 kg dodecamethylene diamine and 4.201 kg of 2-methyl pentamethylene diamine, 1.3 grams DCB antifoam agent and an additional 4.55 kg of water. The resultant

mixture was agitated at 15 rpm. The mixture was heated to 240°C with the vent pressure set at 1.72 MPa. The pressure was then reduced to atmospheric pressure over a period of 60 minutes, the temperature increasing to 275°C. The pressure was then reduced below atmospheric pressure, to 40kPa, over 15 minutes and then maintained for 30 minutes. The polymer obtained was melt extruded, quench, cooled and pelletized. The 12,6/D,6 obtained had an IV (measured in m- cresol) of 1.25 and an RV (Relative viscosity, measured in formic acid) of 61. The DSC scan of this copolyamide was identical with that shown in Figure 1.

TABLE IV

Run No.	Mole Ratio 12,6/D,6	% Yield	Melting Point (°C)	Inherent Viscosity	$-NH_2$	-COOH
1	10/90	97.0	180.0 (145.3)	0.76	122.2	105.9
2	20/80	92.6	174.1 (149.2)	0.69	162.5	98.7
3	30/70	94.0	170.3 (141.0)	0.67	191.0	93.9
4	40/60	93.5	178.7	0.85	102.7	101.4
5	50/50	93.7	186.7	0.82	118.0	100.7
6	70/30	92.9	199.1 (210.4)	1.11	73.0	64.4
7	100/0	96.2	235 (215)	1.39	20.9	78.9

Note: Melting temperatures in brackets were minor peaks on DSC curve.

Example V

The procedures described above in Example IV were also used for the preparation of low melting homopolyamides of branched diamines and long chain aliphatic diacids. It was found that a homopolymer of 2-methyl pentamethylene diamine and sebacic acid (D,10) had a major melting peak at 165°C; the melting profile of the polymer is given in Figure 2. A homopolymer of 2-methyl-pentamethylene diamine and 1,12 dodecane dicarboxylic acid (D,12) had a major melting peak at 143°C; the melting profile of the polymer is given in Figure 3. Both of these homopolyamides satisfy the requirements of low temperature heat sealable nylon.

Examples of thermal transitions of both low temperature polyamides and of "regular" higher temperature polyamides are given in Table V. In Table V, Delta H-1 is the heat of fusion and is an indication of the amount of crystallinity in the polymer; Delta H-2 is the heat of crystallization. The polymers that are heat sealable at low temperatures are indicated.

TABLE V

Polymer	Composition (mole %)	Melting Point (°C)	Delta H-1 (J/gm)	Crystallization Temp. (°C)	Delta H-2 (J/gm)
12,6/D,6	10/90	180.0	50.2	120.0	20.5
12,6/D,6	20/80	174.1	54.8	117.6	8.8
12,6/D,6	30/70	170.3	61.2	123.9	22.9
12,6/D,6*	40/60	178.7	88.6	145.8	38.6
12,6/D,6	50/50	186.7	87.0	158.8	40.5
12,6/D,6	70/30	199.1	66.1	181.4	41.2
12,6	100	235.5	102.6	204.5	51.0
6,12	100	216.5	74.5	186.7	64.4
D,6	100	184			
D,10*	100	165	51.8	120.5	38.8
D,12	100	143	44.8	112.4	4.0
10,6/D,6*	40/60	176.8	51.4	157	43.7
6,6	100	265	192**	235	
Nylon 6	100	218	71.3		

Note: * = low temperature polyamides ** = single crystal

Example VI

Oxygen permeability properties of both low temperature polyamide films and that of "regular" polyamide films are given in Table VI. Water vapor transmission rates of the polymers are given in Table VII Generally, commercially available grades of LLDPE film have oxygen transmission rates in the range of about 500 cc-mil/100 in^2/day.

TABLE VI

Polymer	O_2 Permeability (0% Relative Humidity)
D,10	10.9
D,12	15.1
10,6/D,6 (40/60)	4.9
12,6/D,6 (40/60)	11.8
Nylon 6,6	4.3

12,12	86.1

Note: O_2 transmission rate in cc-mil/100 in^2/day, measured according to ASTM D-3985-81. All films were cast films except D,10 and 10,6/D,6, which were compression molded.

TABLE VII

Polymer	H_2O Transmission Rate
D,10	6.7
D,12	5.9
10,6/D,6 (40/60)	24.2
12,6/D,6 (40/60)	26.5
Nylon 6,6	49.2
LLDPE	1.0

Note: H_2O vapor transmission rate in g-mil/100 in^2/day, measured according to ASTM F-1249.90. All films were cast films except D,10 and 10,6/D,6, which were compression molded.

The permeability results indicate that the homopolyamides represented by D-10 and D-12, and the copolyamides represented by 12,6/D,6 and 10,6/D,6, both at 40/60 mole per cent, have adequate barrier properties for many heat seal film applications.

Example VII

Pellets of a homopolymer of 2-methyl-pentamethylene diamine and sebacic acid (D,10) were dry-blended with pellets of other polymers as indicated in TABLE VIII. The resulting blends were melt extruded in a 2.0 cm Welding Engineers twin-screw extruder, with non-intermeshing, counter-rotating screws, and having an L/D of about 60. The melt was processed at 230°C using a 58 micron screen. A vacuum was applied to the vent port. The melt was then extruded through a 15 cm flat film die. The extrudate was quenched on a chill roll set at a temperature of 15°C to form a film having a thickness of between 89 and 102 microns. The D,10 polymer had a relative viscosity of 54 (in formic acid) and a melting point of 164°C.

Heat seal and hot tack tests were carried out on these films. The results reported in TABLE VIII show the heat-seal initiation temperature, as well as the maximum recorded heat seal strength. Similar data is reported for hot tack. TABLE VIII also reports oxygen permeability test results on these films.

Blocking properties were examined visually after two weeks and the values reported in TABLE VIII were assigned based on the following scale:

1 = none or very slight blocking such that the film unwound easily

2 = slight blocking such that there was infrequent sticking between adjacent layers of wound film

2.5 = moderate blocking such that there was frequent sticking between adjacent layers of wound film thereby causing the film to be difficult to unwind

3 = severe blocking such that the film could not be unwound from a roll

Additionally, in TABLE VIII the following abbreviations were used:

"g-PE" = 1% by weight maleic anhydride grafted polyethylene having a melt index of 4.2 prepared by grafting maleic anhydride onto an ethylene/butene linear low density ~~polyethylene having a density of 0.920 g/cc~~

"Ionomer" = Surlyn® AD8270 which was commercially available from E.I. du Pont de Nemours and Company

"Selar®" = Selar® OH 3003 which was commercially available from E.I. du Pont de Nemours and Company

TABLE VIII

Composition	Block-ing	Heat-Seal *		Hot-Tack *		O_2 Permeability at 0% relative humidity and 23°C (cc-mil/100 in²/ day)
		Init-iation Temp. (°C)	Max. Seal Strength(g/cm)	Init-iation Temp. (°C)	Max. Seal Strength (g/cm)	
D,10 Control	3	<66	2183	<69	184	21.4
D,10 + 20 wt% g-PE	1	<66	2864	<69	184	22.0
D,10 + 20 wt% Ionomer	1.5	<66	2362	<69	184	34.4
D,10 + 30 wt% Selar®	1	<66	1792	<69	184	10.4

Note: * Heat-seal and hot-tack were not tested below 90 C jaw set-point temperature (equivalent to 66 C heat-seal interface temperature, and 69 C hot-tack interface temperature). Therefore, if good sealing was shown at this temperature, then the actual seal-initiation temperature is somewhere below this value. All temperatures in the table above were converted from jaw set-point temperature values to film seal interface values.

The results shown in TABLE VIII indicate that the addition of a second polymer reduces film blocking of the base resin without sacrificing heat-sealing properties.

Example VIII

Pellets of a homopolymer of 2-methyl-pentamethylene diamine and sebacic acid (D,10) were dry-blended with pellets of other polymers as indicated in TABLE IX. The resulting blends were melt extruded in a 2.0 cm Welding Engineers twin-screw extruder, with non-intermeshing, counter-rotating screws, and having an L/D of about 60. The melt was processed at 280°C using a 58 micron filter screen. A vacuum was applied to the vent port. The melt was then extruded through a 15 cm flat film die. The extrudate was quenched on a chill roll set at a temperature of 15°C to form a film having a thickness of between 89 and 102 microns. The D,10 polymer had a relative viscosity of 54 (in formic acid) and a melting point of 164°C.

Heat seal and hot tack tests were carried out on these films. The results reported in TABLE IX show the heat-seal initiation temperature, as well as the maximum recorded heat seal strength. Similar data is reported for hot tack. TABLE IX also reports oxygen permeability test results on these films. Blocking values were recorded based on the scale above.

Additionally, in TABLE IX the following abreviations were used:

"nylon 6,6" = unreinforced nylon 6,6 resin having a relative viscosity of 52 in formic acid

"nylon 6" = BS 700A nylon 6 resin which was commercially available from BASF

TABLE IX

Composition	Blocking	Heat-Seal * Initiation Temp. (°C)	Heat-Seal * Max. Seal Strength (g/cm)	Hot-Tack * Initiation Temp. (°C)	Hot-Tack * Max. Seal Strength (g/cm)	O_2 Permeability at 0% relative humidity and 23°C (cc-mil/100 in²/ day)
D,10 Control	2.5	78	179	<69	184	24.2
D,10 + 30 wt% nylon 6,6	2	<66	250	<69	184	17.4

D,10 + 30 wt% nylon 6	2			74	184	15.8

NOTE: *Heat-seal and hot-tack were not tested below 90°C jaw set-point temperature (equivalent to 66°C heat-seal interface temperature, and 69°C hot-tack interface temperature). Therefore, if good sealing was shown at this temperature, then the actual seal-initiation temperature is somewhere below this value. All temperatures in the table above were converted from jaw set-point temperature values to film seal interface values.

The results reported in TABLE IX indicate that the addition of a second polymer reduces film blocking of the base resin without sacrificing heat-sealing properties. Heat-seal tests were not carried out on the film made from the D,10/nylon 6 (70/30) blend.

WHAT IS CLAIMED IS:

1. A heat-sealable polyamide film formed from a polyamide comprising:

(a) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and

(b) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl brachnes, if any, within at least two amide lingages along the polymer backbone.

2. A heat-sealable polyamide film as recited in Claim 1, wherein the polyamide is prepared from:

(a) at least one dicarboxylic acid and at least one diamine, wherein said dicarboxylic acid or said diamine or both contain at least one alkyl branch having one to three carbon atoms; and wherein said dicarboxylic acid or said diamine or both comprise at least seven methylene groups; or

(b) at least one alpha omega amino alkyl carboxylic acid, having the formula of $H_2N-R(1)-COOH$, in which R(1) is an aliphatic moiety having at least six methylene groups and at least one pendant alkyl branch having 1 to 3 carbon atoms; or

(c) at least one diamine and at least one nitrile selected from the group consisting of alpha omega amino alkylene nitriles and alpha omega alkylene dinitriles, wherein said diamine or said nitrile or both contain at least one alkyl branch having one to three carbon atoms; and wherein said diamine or said nitrile or both comprise at least seven methylene groups; or

(d) mixtures of any of the monomers described in (a)-(c)).

3. A heat-sealable polyamide film as recited in Claim 2

having a heat seal initiation temperature of less than about 140°C.

4. A heat-sealable polyamide film as recited in Claim 3 having a heat seal strength of greater than about 50 g/cm.

5. A heat-sealable polyamide film as recited in Claim 4 having a hot tack strength of greater than about 10 g/cm.

6. A heat-sealable polyamide film as recited in Claim 5 having a hot tack initiation temperature of less than about 170°C.

7. A heat-sealable film formed from a blend comprising:

(a) at least one polyamide comprising:

(i) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and

(ii) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbond; and

(b) at least one polymer selected from the group consisting of polyamides, vinyl polymers, graft functionalized C_2-C_{20} alpha-olefin polymers, ethylene/ethylenically unsaturated carboxylic acid copolymers, and ionomers.

8. A heat-sealable film as recited in Claim 7 having a heat seal initiation temperature of less than about 140°C.

9. A heat-sealable polyamide film as recited in Claim 8 having a heat seal strength of greater than about 50

g/cm.

10. A heat-sealable polyamide film as recited in Claim 9 having ahot tack strength of greater than about 10 g/cm.

11. A heat-sealable polyamide film as recited in Claim 10 having a hot tack initiation temperature of less than about 170°C.

12. A packaging material comprising a heat-sealable polyamide film as recited in any one of Claims 1-11.

13. A layer in a multilayered structure, said layer comprising a polyamide which comprises:

(a) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and

(b) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone.

14. A coating in a packaging material, said coating comprising a polyamide which comprises:

(a) at least one pendant alkyl branch having 1 to 3 carbon atoms within at least two amide linkages along the polymer backbone, and

(b) at least one sequence of at least seven consecutive carbon atoms, excluding carbon atoms in pendant alkyl branches, if any, within at least two amide linkages along the polymer backbone.

15. A container comprising a heat-sealable polyamide film as recited in Claim 1.

16. A container as recited in Claim 15, wherein the container is in the form of a pouch.

17. A container as recited in Claim 15, wherein the container is in the form of a bag.

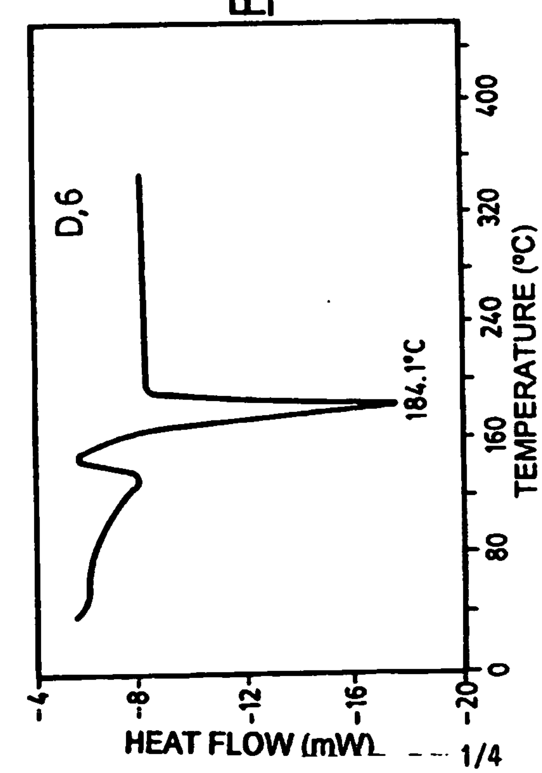


FIG.1a

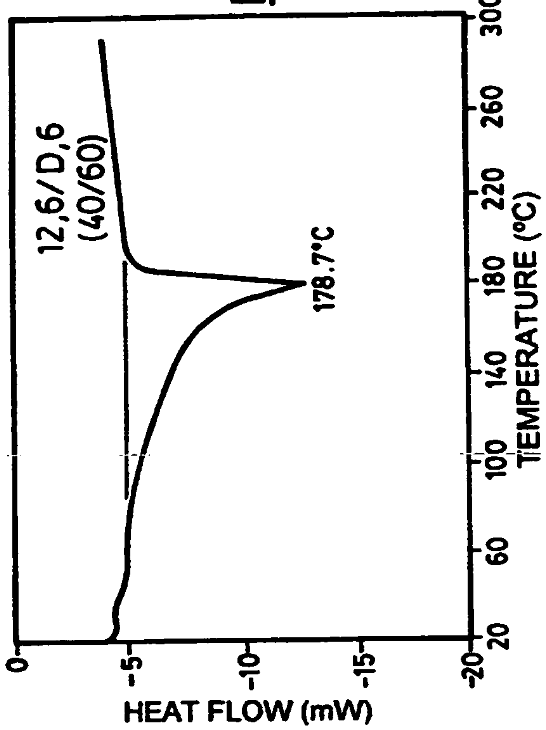


FIG.1b

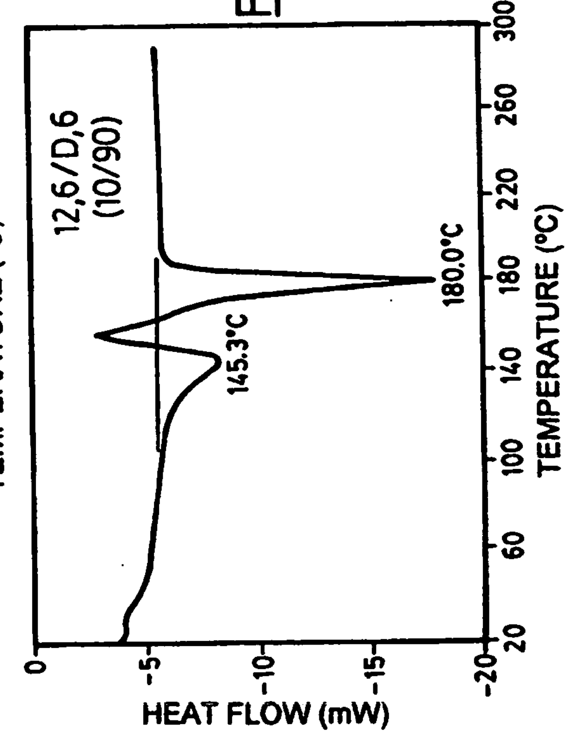


FIG.1c

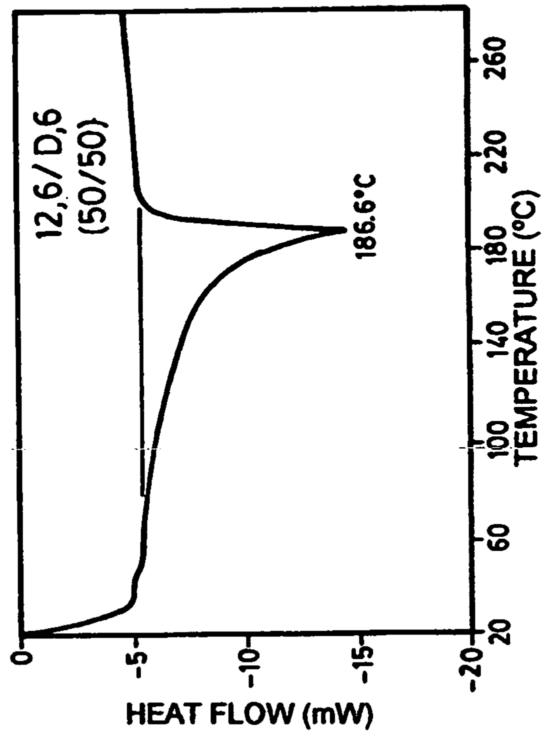


FIG.1d

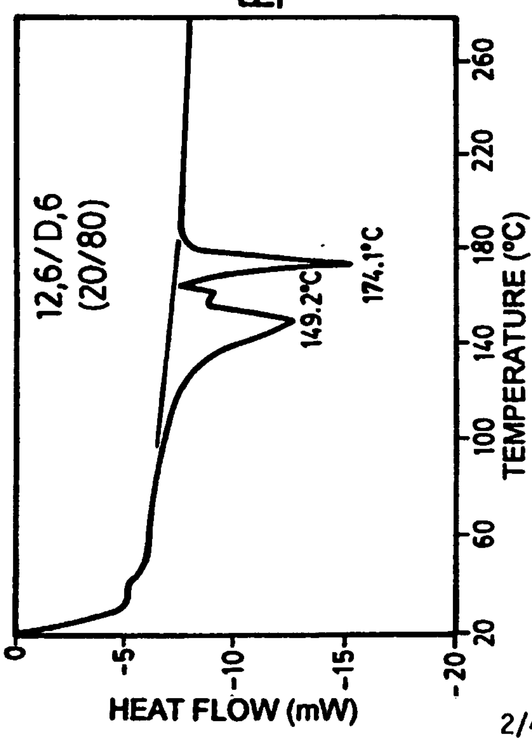
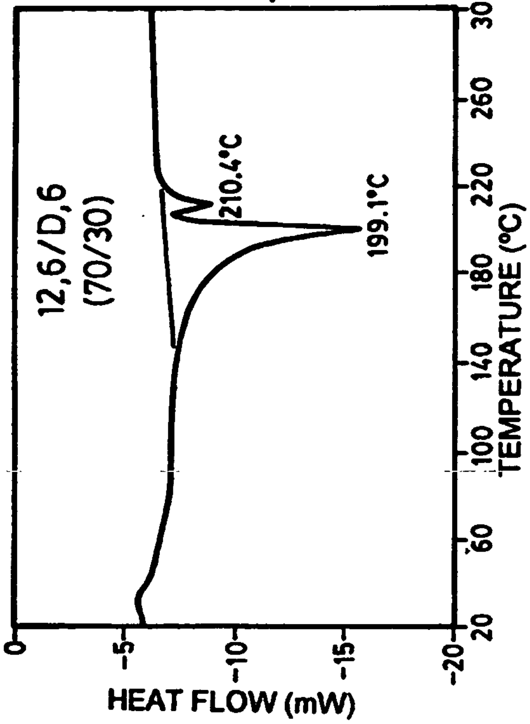


FIG.1e



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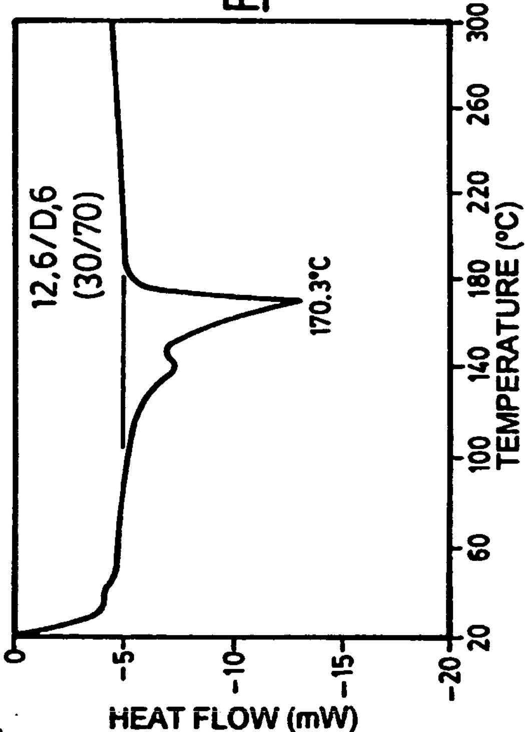


FIG.1g

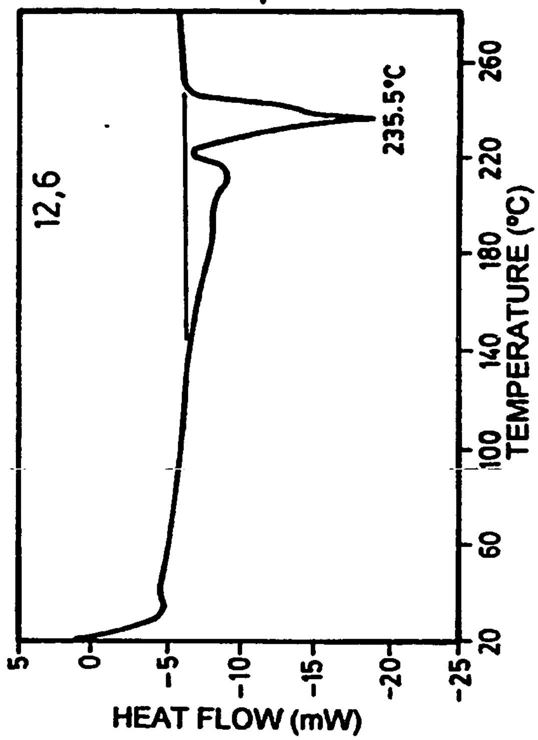
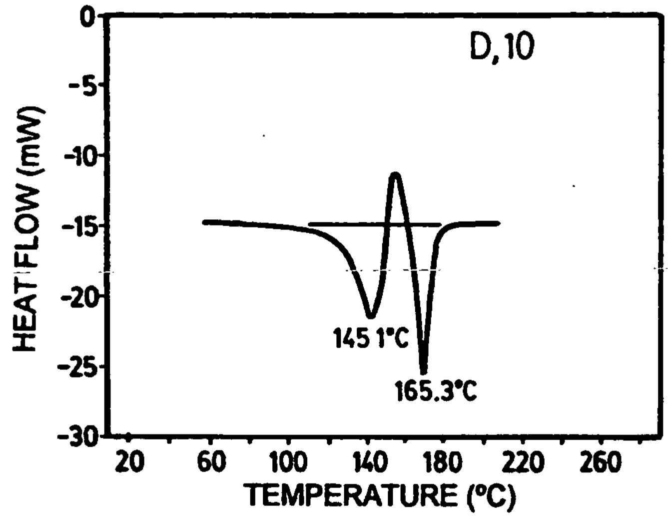


FIG.1h


D,10
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-5
-10
-15
-20
-25
-30
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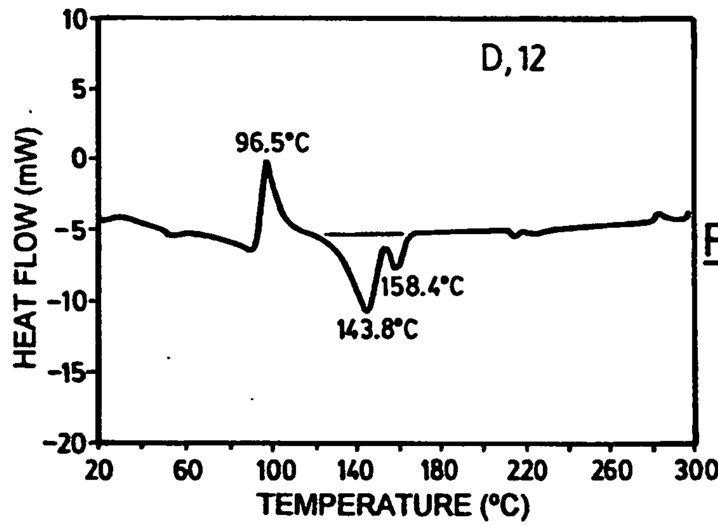
165.3°C
20
60
100
140
180
220
260
TEMPERATURE (°C)

FIG.2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-15
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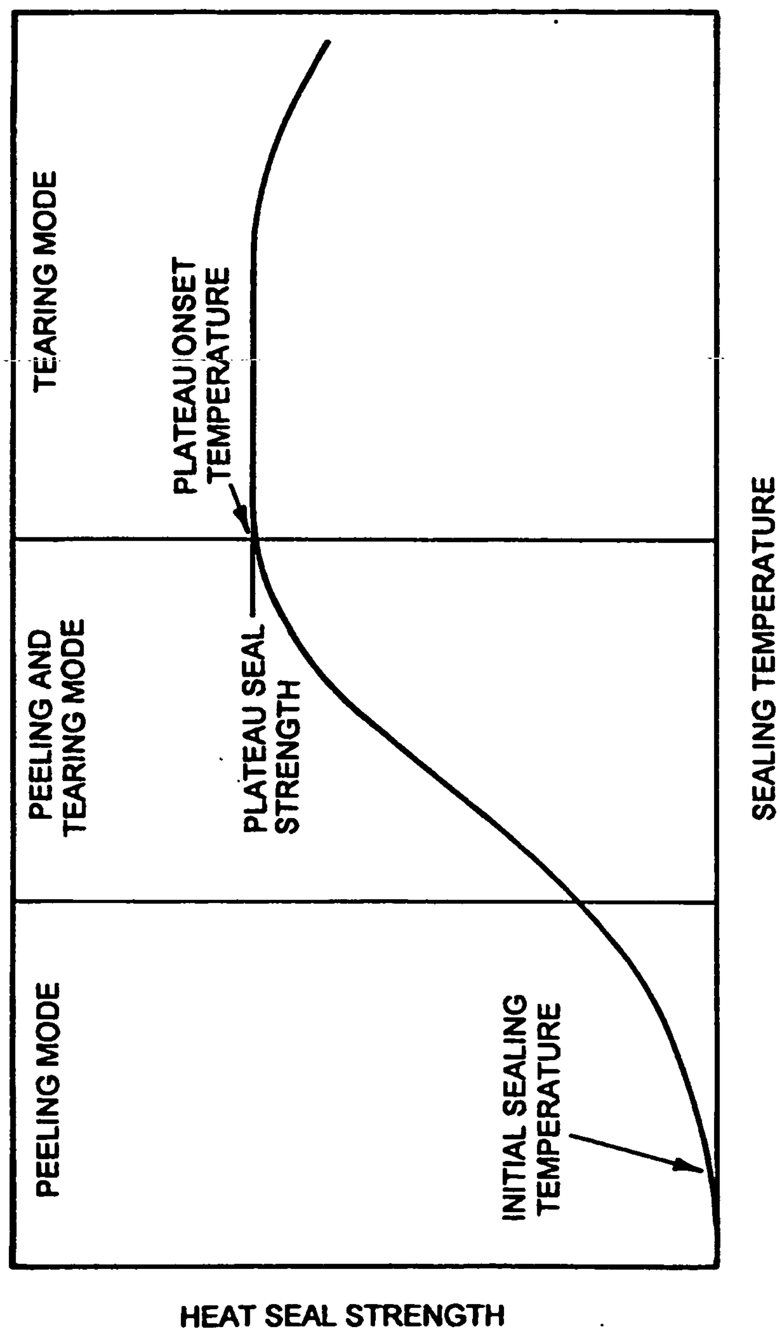
143.8°C
20
60
100
140
180
220
260
300
TEMPERATURE (°C)

FIG.3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PLATEAU ONSET TEMPERATURE
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INITIAL SEALING TEMPERATURE
SEALING TEMPERATURE
HEAT SEAL STRENGTH

FIG. 4

INTERNATIONAL SEARCH REPORT

Inten nal Application No
PCT/CA 94/00667

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G69/26 C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 12194 (DU PONT CANADA) 23 July 1992 cited in the application	
A	WO,A,93 00384 (DU PONT) 7 January 1993	
A	WO,A,93 00385 (DU PONT) 7 January 1993	
A	GB,A,2 006 797 (CIBA.GEIGY) 10 May 1979	
A	GB,A,1 129 466 (EASTMAN KODAK) 9 October 1968	
A	EP,A,0 467 688 (DU PONT) 22 January 1992 see claims 1,3	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
21 April 1995	24.05.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Leroy, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/CA 94/00667

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